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Intermolecular Insertion of Ethylene and Octene into a Palladium−Amide Bond. Spectroscopic Evidence for an Ethylene Amido Intermediate

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Additions to olefins comprise some of the most utilized catalytic reactions.[1] Many of these reactions occur by transfer of a hydride or an alkyl group from a transition-metal complex to a coordinated alkene in a reaction commonly termed migratory insertion.[2] Migratory insertion of an olefin into a transition metal−amide bond is much less established but has been proposed to occur during several classes of palladium-catalyzed reactions, including carboaminations,[3] oxidative aminations,[4] diaminations,[5] aminoacetoxylations,[6] chloroaminations,[7] and hetero-Heck type transformations.[8] Stereochemical evidence for *syn*-aminopalladation by migratory insertion has been gained during studies of some of these catalytic reactions,[3−6,9] but intermolecular insertion of an unactivated alkene into an isolated palladium−amido complex has not been reported.[10,11]

Here, we describe a series of palladium diarylamido complexes that react with unactivated alkenes, including the simplest alkene, ethylene, to form enamine products from initial intermolecular insertion. The stereochemistry of the enamine products, along with kinetic data, supports a migratory insertion pathway, and we have obtained spectroscopic evidence at −100 °C for an ethylene amido intermediate that undergoes migratory insertion at −40 °C.

The preparation of the palladium−amido complexes in this study (**2a**−**e**) is depicted in Figure 1. To generate complexes that are isoelectronic with the rhodium amido complexes reported previously by our group to insert alkenes,[11] an anionic ancillary ligand is necessary. To encourage monomeric structures and to discourage C−N reductive elimination from unsaturated arylpalladium amido complexes,[12] a cyclometalated complex generated from a hindered benzylic phosphine was studied. The stable THF-ligated Pd−amido complexes **2a**−**d** were formed from the reaction of $[(P-C)PdCl]_2$ (**1**) with $KNAr_2$ in THF. Complex **2e** was synthesized by proton transfer between **2a** and $HN((3,5\text{-}CF_3)_2C_6H_3)_2$. The bound THF in **2a**−**e** was evidenced by broad resonances in the ^{1}H NMR spectrum between δ 3.56−3.32 and 1.35−0.94 ppm that integrated to 1 equiv of THF in C_6D_6. Apparently, the bulky *tert*-butyl groups and the weak basicity of the diarylamido nitrogen inhibit formation of an *N*-bridged amido dimer.

An ORTEP diagram of **2a** is shown in Figure 1. Complex **2a** possesses a square planar geometry, and the substituents on the diarylamide lie on either side of the square plane. The Pd−N distance is within error of that of a related three-coordinate diarylamide[12] and the average for palladium−amido complexes (2.083 Å) in the CCD. The Pd−C bond is only ∼0.03 Å longer than that in the previous arylpalladium diarylamido complex. The P−Pd−C angle (82.4°) is typical for a five-membered palladacycle.

Amido complexes **2a**−**e** reacted with alkenes to form enamine products, and the yields and rate constants for these reactions are shown in Table 1. The reaction of **2a** with ethylene for 2 h at −10 °C formed the *N*-vinyldiarylamine product in 89% yield. The reaction of **2a** with neat 1-octene at 80 °C for 30 min generated a mixture of three isomeric enamines in 74% yield. Reactions with 1-octene were conducted in both polar and nonpolar solvents, including diethyl ether, DMF, benzene, and toluene; the highest yields were obtained from reactions in toluene or benzene.

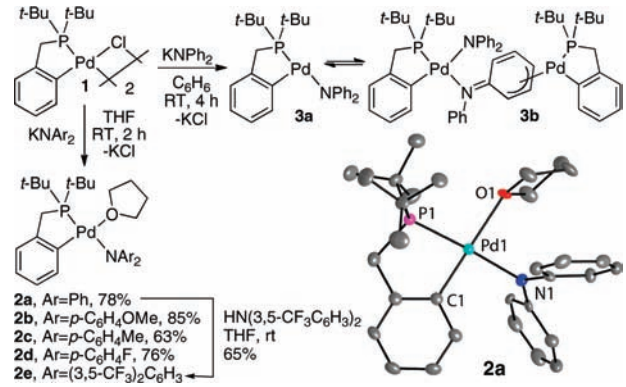
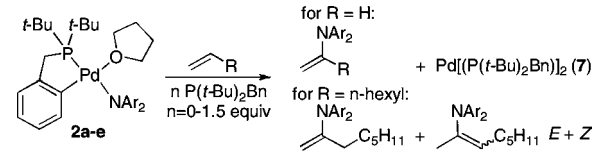


Figure 1. Preparation of THF ligated amido complexes, and an ORTEP drawing of **2a** with 35% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond angles (degrees) and lengths (Å): P−Pd−C, 82.4(2); P−Pd−N, 176.5(2); C−Pd−N, 94.2(2); N−Pd−O, 85.8(2); P−Pd−O, 97.59(9); C−Pd−O, 179.4(2); Pd−C, 2.001(5); Pd−P, 2.249(1); Pd−N, 2.082(2); Pd−O, 2.264(3).

Table 1. Reactions of Ethylene and 1-Octene with Amides **2a**−**2e**[a]



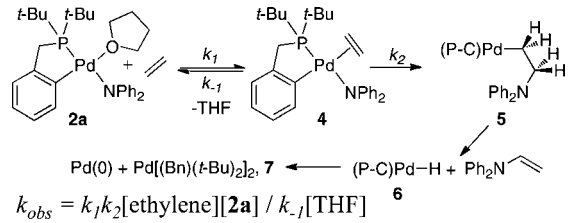
entry	complex	For R = H (yield)	for R = H $k_{obs} \times 10^3$ (s^{-1})	For R = C_6H_{13} (Yield)[b]
1	**2a**	89%	0.91	(neat) 74%
2	**2a**	−	−	(25 equiv) 69%
3	**2a**	−	−	(10 equiv) 48%
4	**2b**	94%	9.6	97%
5	**2c**	63%	4.3	64%
6	**2d**	60%	0.79	52%
7[c]	**2e**	98%	0.053	ND[d]

[a] Conditions for reactions with 1-octene: benzene, 80 °C for 30 min. Conditions for reactions with ethylene: toluene, −10 °C for 2 h, 20 equiv of ethylene. [b] Combined yield for all enamine isomers. [c] Reaction at 85 °C. [d] This reaction did not form detectable amounts of the enamine product.

The data in Table 1 show that the complexes containing the more electron-donating amido groups occurred faster than those containing the less electron-donating amido groups. Complex **2b** containing the most electron-donating di-*p*-ansiylamido ligand reacted approximately 2 times faster than complex **2c** containing di-*p*-tolylamido groups and 10 times faster than complexes **2a** and **2d** containing the less electron-donating diphenyl and *p*-fluorophenylamido ligands. Likewise, complexes **2a** and **2d** reacted much faster than complex **2e** containing the bis-trifluoromethyl-substituted diarylamido ligand.

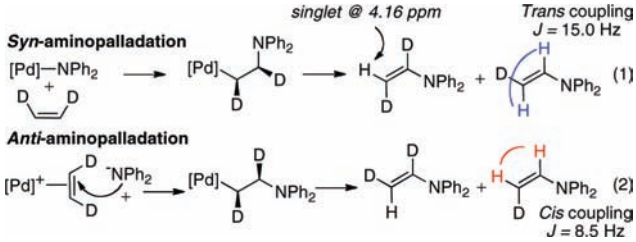
10.1021/ja102172m

Scheme 1



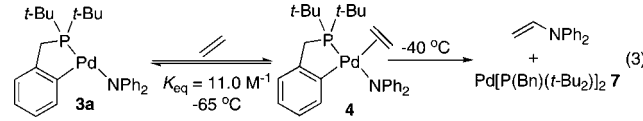
The mechanism of the reaction of ethylene with the amido complexes was examined by kinetic experiments and an evaluation of the stereochemistry of insertion. The decay of diphenylamide **2a** was monitored during reaction with ethylene at −10 °C by ^{1}H NMR spectroscopy. An exponential decay of [**2a**] was observed, indicating a first-order dependence on [**2a**] and reaction through the observed monomer. The reaction was first-order in [ethylene] and inverse first-order in [THF]. These data are consistent with exchange of ethylene for THF and reaction through a four-coordinate alkene complex, as summarized in Scheme 1.

To distinguish between *syn*-aminopalladation by migratory insertion within the amido olefin complex **4** and *anti*-aminopalladation by alternative pathways, the isomeric composition of the products from the reaction of **2a** with *cis*-ethylene-d_2 was examined. The products of *syn*- and *anti*-aminopalladation are distinguishable by the presence or absence of *trans* or *cis* ^3J vicinal coupling constants in the enamine and the chemical shift of the uncoupled proton, as shown in eqs 1 and 2. The terminal vinylic protons of the fully protiated enamine product resonated in the ^{1}H NMR spectrum as doublets at δ 4.21 and 4.16 ppm with J = 15.0 and 8.5 Hz. The product of the reaction of **2a** with *cis*-ethylene-d_2 formed a 72 ± 5:28 ratio of d_2:d_1 *N*-vinyldiphenylamines in 75% yield, reflecting an isotope effect for the β-hydrogen elimination step of 2.7 ± 0.6. In this mixture of product isotopomers, one proton resonated at δ 4.21 as a doublet with a *trans*-coupling of 15 Hz, and one resonated at δ 4.16 ppm as a singlet.[13] These data are consistent with formation of the *Z*-d_2 and *E*-d_1 products in eq 1, and the formation of these stereoisomers is consistent with reaction by a concerted migratory insertion, followed by β-hydrogen elimination from a syn coplanar intermediate.



The analogous diarylamido complex **3a** lacking a bound THF was prepared by the reaction of [(P−C)PdCl]$_2$ (**1**) with KNPh$_2$ in benzene (Figure 1 top). At room temperature, this complex is the three-coordinate **3a**, as revealed by the single ^{31}P resonance at δ 101.8 ppm and a simple ^{1}H NMR spectrum containing one set of aryl resonances. However, at low temperatures, a mixture of this three-coordinate monomer and a dinuclear species (**3b**) was observed by ^{1}H and ^{31}P NMR spectroscopy. The structure of the dinuclear species was identified in the solid state by X-ray diffraction. The three-coordinate amido complex reacted with ethylene at −40 °C to generate enamine products in 86% yield. The rate of this insertion and subsequent β-hydrogen elimination to form enamine is remarkably fast, considering the dearth of olefin insertions into transition metal−amido complexes, but modest computed barriers were reported recently for insertions into a rhodium amide.[14]

Addition of varying excess amounts of alkene to THF-free complex **3a/b** below −40 °C generated a solution for which the NMR spectrum implied a rapidly equilibrating mixture of **3a** and an olefin adduct, formulated as the olefin amido complex **4** in eq 3. Addition of increasing amounts of ethylene at −65 °C led to a progressive upfield shift of the ^{31}P NMR resonance from δ 101.8 ppm for **3a** to δ 90.6 ppm. At −100 °C, distinct signals for the free complex **3a** and olefin adduct **4** were observed, along with 34% of the dinuclear species **3b**. The ^{13}C NMR spectrum of this species generated at −100 °C from $^{13}CH_2$=$^{13}CH_2$ consisted of a broad ^{13}C resonance at 106.5 ppm, which falls in the range of chemical shifts typical for Pd(II) alkene complexes.[15] An equilibrium constant between **3a** and **4** of 11 M^{-1} at −65 °C was determined from a plot of the ^{31}P NMR chemical shift vs the concentration of added ethylene.[16] The rate constant for the decay of the observed species and formation of the enamine at −40 °C was 8.7 × 10^{-4} s^{-1} ($\Delta G^{\ddagger}$ of 17 kcal/mol).



In summary, we have reported the first evidence for intermolecular migratory insertion of alkenes into the Pd−N bonds of discrete Pd-amides. These reactions occur by reversible generation of four-coordinate amido alkene complexes by replacement of bound THF or direct coordination to a three-coordinate amido complex. Complexes of electron-rich amides insert much faster than those of electron-poor amides, and the insertion step itself occurs within minutes, even at −40 °C. Computational studies of the barriers and efforts to design catalytic processes with alternative ancillary ligands are in progress.

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Supporting Information Available: Experimental procedures and characterization of complexes and insertion products. This material is available free of charge via the Internet at http://pubs.acs.org.

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